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2,4-Dinitrophenylhydrazine-Coated Silica Gel Cartridge Method for Determination of Formaldehyde in Air Identification of an Ozone Interference

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16. ABSTRACT

Two versions of the 2,4-dinitrophenylhydrazine method, a coated silica gel cartridge (solid) and acetonitrile impinger (solvent based), were used simultaneously to sample varied concentrations of ozone (0-770 ppb) and formaldehyde (20-140 ppb). Ozone was found to be a negative interference in the determination of formaldehyde by the 2,4-dinitrophenylhydrazine-coated silica gel cartridge method. At 120 ppb of ozone, formaldehyde at 40 ppb was under-reported by the cartridge method by 34% and at 300 ppb of ozone, formaldehyde measurements were 61% low. Greater losses were seen at higher ozone concentrations. Impinger sampling (2,4-DNPH in acetonitrile) showed no formaldehyde losses due to ozone.

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COMMUNICATIONS

2,4-Dinitrophenylhydrazine-Coated Silica Gel Cartridge Method for Determination of Formaldehyde in Air: Identification of an Ozone Interference

Robert R. Arnts*,† and Silvestre B. Tejada‡

Gas Kinetics and Photochemistry Research Branch and Mobile Source Emissions Research Branch, Atmospheric Research and Exposure Assessment Laboratory, United States Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Introduction

We have identified and quantitated substantial negative inteference due to ozone in the determination of formaldehyde in air by the 2,4-dinitrophenylhydrazine- (2,4-DNPH-) coated silica gel cartridge (SGC) technique of Tejada (*1*). 2,4-DNPH acetonitrile solutions in impingers do not exhibit this interference.

The first indication of an interference appeared when we used the 2,4-DNPH-SGC to measure HCHO in the presence of high O_3 concentrations in a study conducted at the University of North Carolina outdoor environmental (smog) chamber facility (Harvey Jeffries, personal communication). Cosampling was conducted with four continuous HCHO analyzers that were based on different analytical methods (*2*). All five methods accurately measured HCHO standards in the absence of O_3. However, when O_3 exceeded 500 ppb, the HCHO data obtained by the 2,4-DNPH-SGC method displayed increasing divergence from the data obtained by the other methods. Because no O_3 interference testing has been reported for any of the solid sorbent methods, and very limited O_3 testing of aqueous 2,4-DNPH systems (*3*, *4*), we initiated a systematic study of the accuracy of the 2,4-DNPH-SGC method for the measurement of HCHO in the presence of cosampled O_3.

Experimental Section

We constructed a dynamic dilution apparatus that simultaneously delivered 50% ambient air and 50% cleaned ambient (zero) air blended with HCHO or 100% zero air blended with HCHO to two heated glass sampling mani-

† Gas Kinetics and Photochemistry Research Branch.
‡ Mobile Source Emissions Research Branch.

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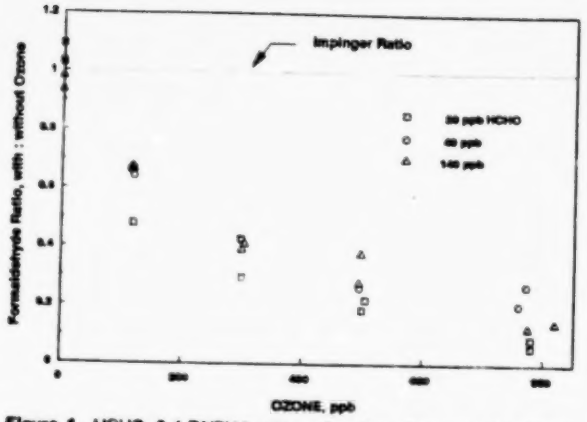

Figure 1. HCHO–2,4-DNPH loss as a function of ozone for silica gel cartridges and impingers. Ratios of formaldehyde (with/without ozone) as a function of added ozone. The cartridges are shown as symbols; the corresponding impinger values are shown as a dotted line.

folds. The gas blends were identical; however, the zero air delivered to one manifold passed through a mercury lamp ozone generator prior to HCHO introduction. Thus, both manifolds provided identical challenge mixtures with respect to HCHO, background O_3, hydrocarbons, etc., but in one manifold, controlled amounts of O_3 could be introduced without photolysis of aldehydes or NO_2. Moisture was not removed from the ambient air, and thus our mixtures reflect ambient air conditions. Each experiment consisted of two cartridges and two impinger samples collected simultaneously at each manifold (cartridges at 1.0 L min^{-1} and impingers at 0.5 L min^{-1}) for 120 min. The 2,4-DNPH-SGCs were prepared according to the procedure of Tejada (*1*). The 2,4-DNPH impinger solutions of 730 mg/L were prepared by dissolving twice recrystallized 2,4-DNPH in distilled-in-glass, HPLC-grade acetonitrile (ACN) and acidifying with $HClO_4$. Cartridges and impinger samples were analyzed by a shortened version of the HPLC procedure described by Tejada (*1*) and by an ACN, H_2O, and CH_3OH program used to check for coeluting peaks.

Sampling was performed in three sets of experiments carried out at nominal HCHO concentrations of 20, 40, and 140 ppb. Thirty-three experiments were performed using 132 cartridges and 132 impinger samples. At each of these levels sampling was performed with increments of O_3 of 0, 120, 300, 500, and 770 ppb above background. The contribution to both sides due to the ambient background range from 0 to 20 ppb of O_3 and from 0 to 3 ppb of HCHO. In addition, 100% zero air and zero air plus HCHO experiments were performed to ascertain the source of unknown HPLC peaks.

Results

Figure 1 is a plot of the ratio of HCHO measured in the presence of additional O_3 to that measured in the presence of only a 0–20 ppb O_3 background as a function of the amount of O_3 added. Each data point represents the ratio of the average of two samples with added O_3 to the average of two samples collected from the reference manifold. The losses observed with the SGCs are quite severe. At 120 ppb of O_3 and ~25 ppb of HCHO between 44% and 52% of the HCHO is not measured. At 300 ppb of O_3 (often seen in severe urban smog episodes), HCHO losses of 57–61% are seen.

In contrast to the cartridge results, the impinger data show no HCHO–2,4-DNPH loss as a function of O_3 over the same experimental conditions. However, we observed accompanying large losses of 2,4-DNPH in both impinger and cartridge samples that were far in excess of losses due to carbonyl to hydrazone conversion. In addition to the O_3 attack on the 2,4-DNPH, we also observed the appearance of new compounds with retention times shorter than HCHO (more polar). These peaks increased in proportion to increasing ozone concentration. Hydrocarbon-free air—ozone experiments demonstrated the same behavior, indicating that the peaks were generated by ozone-sampling media reactions and not by gas-phase ozone–hydrocarbon reactions.

In order to understand the different behavior exhibited by the solvent and solid systems, we loaded impingers and cartridges with approximately equal amounts of acidified 2,4-DNPH and HCHO–2,4-DNPH. In both impingers and cartridges the 2,4-DNPH was completely reacted, while only 54% and 37%, respectively, of the HCHO–2,4-DNPH reacted when exposed to the same amount of O_3.

We also performed a few experiments using the 2,4-DNPH cartridge technique of Kuwata et al. (*5*). They used a C_{18} Sep-Pak cartridge (Waters Associates, Milford, MA), which contains silica gel that has been surface passivated with a nonpolar organic phase. Kuwata et al. used H_3PO_4 to acidify the media (*5*). Our results with this cartridge show that with up to 120 ppb of O_3 (120 L), no O_3 interference is observed with the HCHO–2,4-DNPH. Furthermore, we did not observe the loss of 2,4-DNPH or the formation of the polar products seen in the silica gel and acetonitrile impinger runs. SGCs prepared with H_3PO_4 in place of HCl also showed interference and oxidation products. Thus, these phenomena are apparently substrate dependent and not related to the acid of choice.

Discussion

Ozone will react with 2,4-DNPH and its HCHO hydrazone on the surface of silica gel but not on the nonpolar C_{18} coated silica gel surface; the surface of the solid substrate apparently influences the reactivity of the adsorbed molecules toward ozone. The silica gel is of course a very polar material having OH groups on its surface that present the opportunity for strong hydrogen bonding. The C_{18}-coated silica gel has been rendered nonpolar by the derivatization of the OH groups and hence possesses basically an *n*-paraffinic surface.

Ozone reactions with hydrazines were recently reviewed by Bailey (*6*). Ozonation of hydrazine yielded N_2 and H_2O with small amounts of NH_3 and HNO_3; ozonation of aqueous solutions of hydrazine salts yielded the same products. When 1,1-dimethylhydrazine was ozonated in aqueous solution, N_2, CO_2, and $(CH_3)_2NNNN(CH_3)_2$ were observed. Under acidic conditions no reaction occurred. Another group noted that when 1,1-dimethylhydrazine adsorbed on alumina was ozonated they measured N_2, CO_2, and water (*6*). Atkinson and Carter recently reviewed the gas-phase reactions of ozone with hydrazine, methylhydrazine, and 1,1-dimethylhydrazine (*7*). Both methyl-substituted hydrazines reacted too fast to measure (greater than 1×10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K), while hydrazine reacted at $\sim 3 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. The gas-phase ozone reaction for the formaldehyde hydrazone ($H_2C = NNH_2$) was similar (2.5×10^{-17} cm^3 $molecule^{-1}$ s^{-1}). Bailey also noted one report of ozone reaction with phenylhydrazine and tetraphenylhydrazine, but no products were identified (*6*). Atkinson and Carter proposed that initial O_3 attack on hydrazines could occur by addition to a nitrogen or abstraction of a hydrogen from a weak N–H bond (*7*). Presumably, under acidic conditions O_3 addition to the protonated nitrogen is restricted and hydrogen abstraction is the favored route. They proposed the following

pathway for hydrogen abstraction:

$$RNHNH_2 + O_3 \rightarrow R\dot{N}NH_2 \text{ or } RNH\dot{N}H + O_2 + OH$$

$$R\dot{N}NH_2 \text{ or } RNH\dot{N}H + O_2 \rightarrow RN{=}NH + HO_2$$

$$RN{=}NH + O_3 \text{ or } OH \rightarrow RN{=}\dot{N} + OH + O_2\ (+H_2O)$$

$$RN{=}\dot{N} \rightarrow \dot{R} + N_2$$

We propose that the radicals generated by O_3 attack on 2,4-DNPH on C_{18} substrate are scavenged by the C_{18} and thus limit further attack on 2,4-DNPH or formaldehyde–2,4-DNPH. In contrast the silica gel surface does not present a radical scavenging environment, and hence, the above reactions would be free to propagate, consuming 2,4-DNPH and hydrazone. Furthermore, since the 2,4-DNPH is present on the solid silica gel as an immobilized monolayer, the upstream surfaces (frontal zone) of the cartridge will be depleted of 2,4-DNPH as it is exposed to incoming carbonyls and O_3. Loss of hydrazone in this zone increases as the probability of hydrazone reaction with 2,4-DNPH + O_3 radical products increases.

The results observed in the impingers are consistent with the above results. The acetonitrile is probably not an effective free-radical scavenger since its rate constant with OH is roughly $^1/_{1000}$th that of a C_{10} or greater *n*-alkane (*8*). Therefore the 2,4-DNPH–acetonitrile system probably more closely resembles the silica gel system rather than the C_{18} system. However, the loss of 2,4-DNPH in the impinger is not accompanied by loss of the formaldehyde hydrazone as long as 2,4-DNPH $\gg$ HCHO–2,4-DNPH. In contrast to the silica gel, where the 2,4-DNPH/hydrazone ratio decreases sharply at the cartridge front, the hydrazone in the impinger is rapidly dispersed in the bulk solution. Since the 2,4-DNPH is present in large excess, the hydrazone is effectively protected from attack by the free radical scavenging action of the 2,4-DNPH.

We do not recommend postsampling adjustment of data to correct for loss due to O_3. Our data are based on sampling at constant levels of HCHO and O_3. In ambient atmospheres both components exhibit temporal variation, which may cause more or less hydrazone loss than steady-state conditions. If most of the O_3 is sampled early in the collection period and the HCHO later, then the hydrazone loss will be less than steady-state conditions; conversely, loss could be more severe if the situation were reversed.

Presently we are evaluating a potassium iodide coated copper tubing inlet to remove O_3 prior to collection with a 2,4-DNPH-coated silica gel cartridge. The results thus far look promising. While we have performed limited evaluation of the C_{18} method of Kuwata et al. (*5*), it does not appear to suffer from O_3 interference at O_3 levels of 120 ppb (120 L). However, we have noted that the some of the non-formaldehyde hydrazones once formed are not retained efficiently on the C_{18} and breakthrough occurs. Also we have observed that ozone interacts with the C_{18} cartridges to produce extraneous HPLC peaks, which elute after formaldehyde.

We recommend the suspension of the use of 2,4-DNPH-silica gel for ambient monitoring unless a carbonyl-passive ozone scrubber is employed. We will present details of the above and further work in a full journal article.

Registry No. 2,4-DNPH, 119-26-6; ACN, 75-05-8; HCHO, 50-00-0; O_3, 10028-15-6.

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